No. 218

# INVESTIGATIONS IN THE DIPHENYL SERIES, PART VIII—DERIVATIVES OF 2-AMINO-AND 4-AMINODIPHENYL

BY

F. BELL

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES
(The Wellcome Foundation Ltd.)
T. A. HENRY, D.Sc., *Director*
6, King Street, Snow Hill
LONDON, E.C. 1

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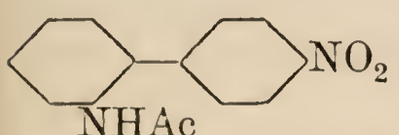
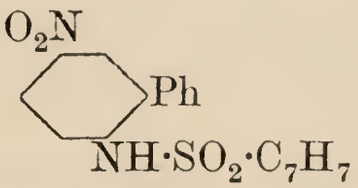
# CCCLXVI.—*Investigations in the Diphenyl Series. Part VIII. Derivatives of 2-Amino- and 4-Amino-diphenyl.*

By Frank Bell.

In view of the anomalous nitration of 2-acetamidodiphenyl, which yields 4′-nitro-2-acetamidodiphenyl (I) as a primary product (Scarborough and Waters, J., 1927, 89), the behaviour of 2-p-*toluenesulphonamidodiphenyl* has been examined (compare J., 1926, 2708; 1927, 1129). This compound nitrates with the greatest ease first in the 5-position (II) and then in the 3-position (III). The same ease of substitution is shown by 4′-*nitro*-2-p-*toluene-sulphonamidodiphenyl*, since under gentle conditions of nitration



(I.)



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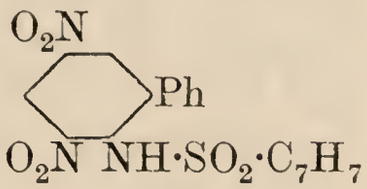
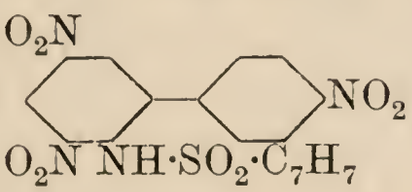
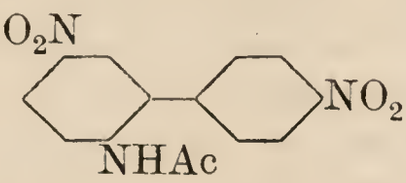


(III.)

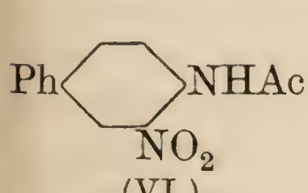
it yields the 3 : 5 : 4′-*trinitro*-derivative (IV). This behaviour is in marked contrast with that of the acetylated bases, for 5 : 4′-dinitro-2-acetamidodiphenyl (V) can be recovered unchanged after solution in fuming nitric acid. 2-Acetamidodiphenyl itself undergoes nitration less readily than 4-acetamidodiphenyl, but the introduction of a nitro-group can be effected without use of sulphuric

(IV.)


(V.)

acid, and in this case the primary product is the 5-*nitro*-derivative. Further nitration of this, under all the conditions tried, gave 5 : 4′-dinitro-2-acetamidodiphenyl (V) as the only isolable product. This behaviour accords well with the nitration of 4-acetamidodiphenyl, which gives the 3-nitro-derivative (VI) as primary product and then the 3 : 4′-dinitro-derivative (VII) (Scarborough and Waters, J., 1927, 1134), and these results suggested that 4-*p*-toluenesulphonamidodiphenyl should give the 3 : 5-*dinitro*-derivative (VIII) : actually it does nitrate with the utmost ease in the 3 : 5-positions.



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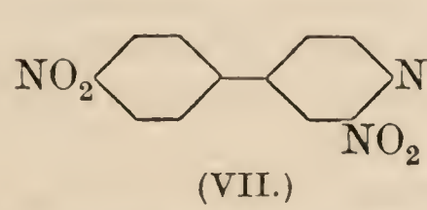
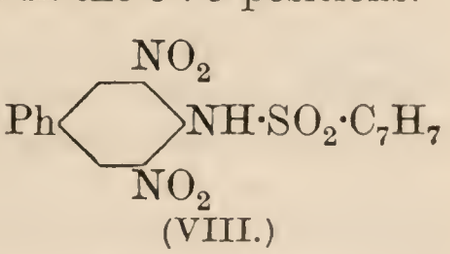


(VII.)



(VIII.)

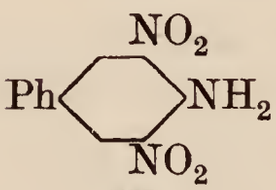
This dinitro-compound (VIII) on hydrolysis readily yields the

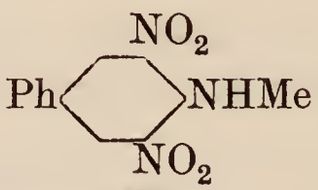
dinitro-base (IX), which is entirely different from the compound to which Fichter and Sulzberger (*Ber.*, 1904, **37**, 878) assigned this constitution. It is more highly coloured and less easily acetylated, and possesses the much greater solubility and lower melting point which compounds with groups in the 3-position invariably show when compared with compounds having the same substituents in the 4′-position.

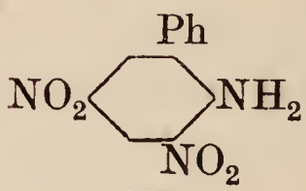
2-p-*Toluenesulphonmethylamidodiphenyl* also nitrates in the 5-position, but since compounds of this type nitrate so much less readily and quantitatively than the corresponding unmethylated derivatives, it is preferable to effect nitration before methylation.

A difficulty in acetylating amines having nitro-groups in positions adjacent to the amino-group has been noticed in this work: 3 : 5-*dinitro*-4-*aminodiphenyl* (IX) and 3 : 5-dinitro-4-methylaminodiphenyl (X) are acetylated only in the presence of sulphuric acid, and the acetyl derivative of 3 : 5-*dinitro*-2-*aminodiphenyl* (XI) has not yet been obtained.

This investigation suggests that the arylsulphonyl group has a

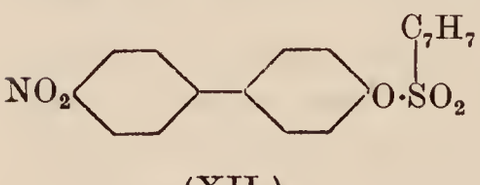

(IX.)

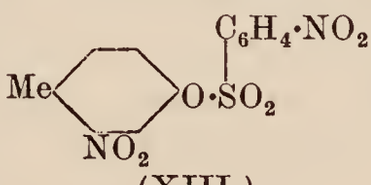

(X.)

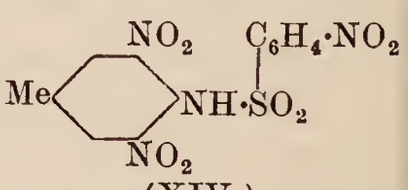

(XI.)

considerable advantage over the acetyl group for the preparation of highly nitrated amines in good yield. In higher nitrations (especially in examinations of a quantitative character) the liability of a nitro-group to enter the *p*-toluenesulphonyl residue has to be guarded against. This difficulty can be overcome by the use of the *m*-nitrobenzenesulphonyl derivative or the *p*-nitrobenzenesulphonyl derivative, which has now been made readily accessible (see p. 2776).

The nitration of the *p*-toluenesulphonyl derivative of 4-hydroxydiphenyl to give the 4′-derivative (XII) is in such marked contrast with the nitration of the corresponding derivative of 4-amino-

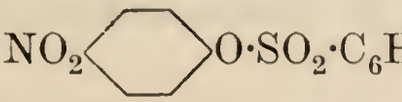

(XII.)

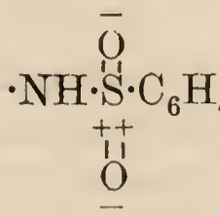

(XIII.)


(XIV.)

diphenyl (above) that the first use of *p*-nitrobenzenesulphonyl chloride has been made in contrasting the behaviour of the derivatives of *p*-cresol and of *p*-toluidine : p-*tolyl* p-*nitrobenzenesulphonate* nitrates in the 2-position (XIII), and p-*nitrobenzenesulphon*-p-*tolylamide* in the 3 : 5-positions (XIV), of the toluene nucleus (Me = 1). That the *p*-nitrobenzenesulphonate group is para-

directing is shown by the nitration of *phenyl* p-*nitrobenzenesulphonate* to give the 4-*nitro*-derivative (XV).

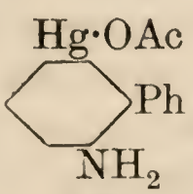
(XV.) 


(XVI.)

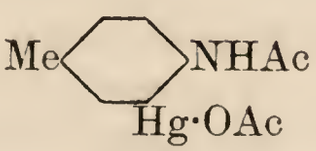
The results outlined above show the powerful orienting nature of the benzenesulphonamido-group, its weakening in the benzenesulphonmethylamido-group, and its complete overthrow in the benzenesulphonates.

It appears that the positively charged sulphur atom of the sulphonamido-group (XVI) facilitates and stabilises the adoption of a negative charge by the nitrogen atom (shown by sodium salt formation), and causes substitution to proceed as in the case of a phenol. The observed sensitiveness of the acetyl group to conditions of nitration can only be explained on the assumption that the acetamido-group enters into salt formation with a strong acid (see, *inter alia*, Dadswell and Kenner, J., 1927, 1102), being thereby converted into a very weakly orienting positive group, so that further substitution naturally resembles that of 2-nitrodiphenyl (Le Fèvre and Turner, J., 1926, 2043; Bell and Kenyon, *ibid.*, p. 2707).

The mercuration of diphenyl derivatives has been little studied, though such mercury compounds would seem to offer a ready source of substances, such as 3-bromo-4-acetamidodiphenyl, otherwise difficult to obtain. A preliminary examination has now been made. 2-Aminodiphenyl monomercurated in the 5-position (XVII), for the product after acetylation and demercuration gave 5-bromo-2-acetamidodiphenyl.


(XVII.)


(XVIII.)


(XIX.)

4-Aminodiphenyl, by analogy with its behaviour on halogenation, must mercurate in the 3-position, but the monomercuri-derivative actually obtained gave 3 : 4′-dibromo-4-acetamidodiphenyl on acetylation and demercuration, a result which is attributed to the fact that, owing to the limited solubility of the mercury compound, the treatment with bromine must take place in hot acetic acid solution.

This observation recalls the ease with which 4-acetamidodiphenyl brominates in the 4′-position (Scarborough and Waters, J., 1926,

557 ; Kenyon and Robinson, *ibid.*, p. 3050) and in view of the results described earlier in this paper it seemed of interest to examine the bromination of 4-*p*-toluenesulphonamidodiphenyl. Under the experimental conditions used, only the 3-*bromo*-derivative could be isolated, and in poor yield.

3-Bromo-4-hydroxydiphenyl gave a *monomercuri*-derivative, and on treatment with bromine this gave 3 : 5 : 4′-tribromo-4-hydroxydiphenyl : the tribromination of 4-hydroxydiphenyl is not easily accomplished in normal circumstances.

The preparation of the above mercurated acetanilides directed attention to the statement that aceto-*p*-toluidide on mercuration behaves abnormally in giving the anhydro-compound (XVIII) (Schrauth and Schoeller, *Ber.*, 1910, **43**, 2808). The preparation of 3-*acetoxymercuriaceto*-p-*toluidide* (XIX) both by direct mercuration and by acetylation of acetoxymercuri-*p*-toluidine is now described.

2-Aminodiphenyl appears to offer a ready means of obtaining the highly interesting hydrocarbon *o*-diphenylene (Dobbie, Fox, and Gauge, J., 1911, **99**, 683; 1913, **103**, 36) by elimination of its diazotised amino-group with copper powder (a method so successful in the preparation of fluorenone derivatives from aminobenzophenones; Ullmann and Mallet, *Ber.*, 1898, **31**, 1694). However, under the conditions of the present experiments 2-chlorodiphenyl and 2-azodiphenyl were the only isolable products.

## Experimental.

2-Aminodiphenyl was prepared in 80% yield by the method of Scarborough and Waters (*loc. cit.*). West's process (J., 1925, **127**, 494) applied to 2-nitrodiphenyl gave a brown 2-aminodiphenyl in only 55% yield.

*Attempted Preparation of* o-*Diphenylene.*—The filtered diazo-solution prepared from 2-aminodiphenyl (17 g.) was poured into a well-stirred copper paste (from copper sulphate, 125—300 g.). From the reaction mass, by distillation in steam, a small quantity of oily 2-chlorodiphenyl was obtained which crystallised after being shaken with hydrochloric acid and with sodium hydroxide; m. p. 33° (Found : C, 76·6; H, 4·5. Calc. : C, 76·4; H, 4·8%). From the residue after steam distillation, ether extracted a gummy substance; extraction of this with cold petroleum left almost pure 2-azodiphenyl, which crystallised from petroleum in orange needles, or from a very concentrated benzene solution in garnet-red prisms, m. p. 144° (Found : C, 86·4; H, 5·7. Calc. : C, 86·2; H, 5·4%).

5-*Nitro*-2-*acetamidodiphenyl.*—To a mixture of nitric acid (*d* 1·5; 20 c.c.) and acetic acid (20 c.c.) was added 2-acetamidodiphenyl (10 g.), the temperature being kept below 30°. After ½ hour, the

solution was poured into water and the precipitated solid was removed and boiled with alcohol. The filtered solution deposited 5-*nitro*-2-*acetamidodiphenyl* in thick orange needles, m. p. 133° (Found : C, 65·3; H, 4·6. $C_{14}H_{12}O_3N_2$ requires C, 65·6; H, 4·7%).

If the temperature is allowed to rise during the nitration, there is formed in addition to the above compound a mixture of more highly nitrated products, which are readily separated owing to their sparing solubility in hot alcohol.

5-*Nitro*-2-*aminodiphenyl*, obtained by hydrolysis of its acetyl derivative with alcoholic hydrochloric acid, crystallised from alcohol in yellow needles, m. p. 125° (Found : C, 66·8; H, 4·6. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7%). The base was readily re-acetylated and converted into its *p*-toluenesulphonyl derivative by the usual methods. 5-*Nitro*-2-p-*toluenesulphonamidodiphenyl* crystallised from acetic acid in thick, pale yellow needles, m. p. 169° (Found : C, 62·2; H, 3·9. $C_{19}H_{16}O_4N_2S$ requires C, 62·0; H, 4·3%).

2-p-*Toluenesulphonamidodiphenyl*, obtained from 2-aminodiphenyl by the usual method, crystallised readily from acetic acid, alcohol, or benzene–petroleum in large rhombs, m. p. 99° (Found : C, 70·6; H, 5·3. $C_{19}H_{17}O_2NS$ requires C, 70·6; H, 5·3%). Methylation yielded 2-p-*toluenesulphonmethylamidodiphenyl*, which crystallised from alcohol in prisms, m. p. 136° (Found : C, 71·2; H, 5·8. $C_{20}H_{19}O_2NS$ requires C, 71·3; H, 5·6%).

*Nitration of* 2-p-*Toluenesulphonamidodiphenyl*.—(*a*) 2·5 G. were warmed on a water-bath for 7 hours with a mixture of water (25 c.c.) and nitric acid (2·5 c.c.). The product, crystallised from acetic acid, gave pure 5-nitro-2-*p*-toluenesulphonamidodiphenyl (see above).

(*b*) To 3·7 g., dissolved in acetic acid (37 c.c.) at 70°, was added nitric acid (*d* 1·5; 3 c.c.) in acetic acid (3 c.c.), and the whole was maintained at 70° for ¼ hour. On cooling, the liquid filled with prisms of 3 : 5-*dinitro*-2-p-*toluenesulphonamidodiphenyl*, m. p. 186°, unchanged after crystallisation from acetic acid (Found : C, 55·5; H, 3·8. $C_{19}H_{15}O_6N_3S$ requires C, 55·7; H, 3·6%). A solution of this compound (2 g.) in sulphuric acid (4 c.c.) was after ½ hour poured into water and neutralised with ammonia; the precipitated 3 : 5-*dinitro*-2-*aminodiphenyl* crystallised from alcohol in lustrous yellow plates, m. p. 182° (Found : C, 55·2; H, 3·6. $C_{12}H_9O_4N_3$ requires C, 55·6; H, 3·5%). This base was recovered unchanged after boiling under reflux for 2 hours with acetic anhydride alone, and in the presence of sulphuric acid only oily products were obtained.

*Nitration of* 2-p-*Toluenesulphonmethylamidodiphenyl*.—(*a*) This

compound (2 g.) was added to a mixture of nitric acid (*d* 1·5; 10 c.c.) and acetic acid (10 c.c.) and after 10 minutes the resultant solution was poured into water. (*b*) 3·5 G. in nitric acid (7 c.c.) were warmed on a water-bath, and the mixture poured into water. The gummy precipitate obtained by either method, when crystallised from acetic acid, furnished pure 5-*nitro*-2-p-*toluenesulphonmethylamidodiphenyl* in rosettes of small needles, m. p. 152° (Found: C, 62·4; H, 4·4. $C_{20}H_{18}O_4N_2S$ requires C, 62·8; H, 4·7%). It was proved identical with the substance obtained by the methylation of 5-nitro-2-*p*-toluenesulphonamidodiphenyl (described above).

4′-Nitro-2-acetamidodiphenyl was prepared and hydrolysed by the method of Scarborough and Waters (*loc. cit.*). 4′-*Nitro*-2-p-*toluenesulphonamidodiphenyl*, prepared from the base in the usual manner, crystallised from acetic acid in very pale yellow needles, m. p. 163° (Found: C, 62·0; H, 4·4. $C_{19}H_{16}O_4N_2S$ requires C, 62·0; H, 4·4%). This compound (1 g.) in warm acetic acid (10 c.c.) was treated with fuming nitric acid (1 c.c.) in acetic acid (1·5 c.c.). On cooling, the liquid filled with crystals which, recrystallised from acetic acid, gave pure 3 : 5 : 4′-*trinitro*-2-p-*toluenesulphonamidodiphenyl* in prisms, m. p. 190° (Found: C, 49·8; H, 3·2. $C_{19}H_{14}O_8N_4S$ requires C, 49·8; H, 3·1%). This trinitro-derivative was hydrolysed by dissolving it in concentrated sulphuric acid and after ½ hour pouring the solution on ice. The precipitated 3 : 5 : 4′-*trinitro*-2-*aminodiphenyl* crystallised from much alcohol as a bright yellow powder, m. p. 229° (Found: C, 47·7; H, 2·9. $C_{12}H_8O_6N_4$ requires C, 47·3; H, 2·6%).

5 : 4′-*Dinitro*-2-*acetamidodiphenyl from* 5-*Nitro*-2-*acetamidodiphenyl*.—To 1 g., dissolved in a mixture of sulphuric acid (3 c.c.) and acetic acid (1·5 c.c.), fuming nitric acid (0·8 c.c.) in acetic acid (1 c.c.) was added. After 12 hours, the solution was poured into water; the precipitate obtained, after being washed with alcohol, crystallised from alcohol–pyridine in prismatic needles, m. p. 208°, identical with the product obtained by the nitration of 4′-nitro-2-acetamidodiphenyl. 5 : 4′-Dinitro-2-aminodiphenyl did not react with *p*-toluenesulphonyl chloride under the ordinary conditions.

*Nitration of* 4-p-*Toluenesulphonamidodiphenyl*.—To 10 g., dissolved in acetic acid (10 c.c.) at 80°, fuming nitric acid (10 c.c.) in acetic acid (10 c.c.) was added. On cooling, pure 3 : 5-*dinitro*-4-p-*toluenesulphonamidodiphenyl* (9·5 g.) separated; it crystallised from acetic acid in long needles, m. p. 189° (Found: C, 55·4; H, 3·7. $C_{19}H_{15}O_6N_3S$ requires C, 55·7; H, 3·6%). Hydrolysis in the usual manner gave 3 : 5-*dinitro*-4-*aminodiphenyl*, which crystallised from benzene in orange-red needles, m. p. 177° (Found: C, 55·6; H, 3·5. $C_{12}H_9O_4N_3$ requires C, 55·6; H, 3·5%). This base was not attacked

by acetic anhydride alone, but in the presence of sulphuric acid it gave 3 : 5-*dinitro*-4-*acetamidodiphenyl*, which crystallised from alcohol in pale yellow needles, m. p. 146° (Found : C, 55·8; H, 3·8. $C_{14}H_{11}O_5N_3$ requires C, 55·8; H, 3·6%).

3 : 5-*Dinitro*-4-p-*toluenesulphonmethylamidodiphenyl*, obtained from the corresponding base by methylation, crystallised from acetic acid in needles, m. p. 144° (Found : C, 55·9; H, 4·3. $C_{20}H_{17}O_6N_3S$ requires C, 56·2; H, 4·0%). Hydrolysis with sulphuric acid gave the already described 3 : 5-dinitro-4-methylaminodiphenyl (Bell and Kenyon, J., 1926, 2710), which with acetic anhydride, in the presence of sulphuric acid, gave 3 : 5-*dinitro*-4-*acetomethylamidodiphenyl*. This substance crystallised from alcohol in lustrous yellow needles, m. p. 149° (Found : C, 57·2; H, 4·0. $C_{15}H_{13}O_5N_3$ requires C, 57·2; H, 4·1%).

3 : 4′-*Dinitro*-4-*acetamidodiphenyl*.—4-Acetamidodiphenyl (5 g.) was added to ice-cold fuming nitric acid (15 c.c.) and after ½ hour the solution was poured on ice. The precipitate, after being washed with alcohol, crystallised from pyridine in pale yellow needles, m. p. 240°. 2 G., when heated under reflux with alcoholic hydrochloric acid (100 c.c.), rapidly dissolved to a clear solution which soon deposited orange needles of 3 : 4′-dinitro-4-aminodiphenyl, readily recrystallised from pyridine. This base did not react with *p*-toluenesulphonyl chloride under the usual conditions.

p-*Nitrobenzenesulphonyl Chloride*.—To a boiling solution of *p*-chloronitrobenzene (250 g.) in alcohol (600 c.c.) was added in portions the product obtained by fusing crystalline sodium sulphide (200 g.) and sulphur (35 g.). The mixture was heated for ½ hour and then cooled to about 50°. The solid product, after being washed with alcohol, water, and again with alcohol, was boiled with acetic acid (500 c.c.), cooled, collected, dried, and divided into 40 g. batches. Each batch was added to fuming nitric acid (10 c.c.), and the solution was warmed for 1 hour, diluted with water (500 c.c.), and filtered. The combined filtrates were evaporated almost to dryness and again after the addition of more water. The residue was neutralised with dilute aqueous ammonia, and ammonium *p*-nitrobenzenesulphonate obtained in large crystals. This ammonium salt (100 g.) was heated with chlorosulphonic acid (100 c.c.) at 100° for 1 hour, and the cooled solution poured on ice. The precipitate was collected rapidly, dried, and crystallised from benzene–light petroleum, from which *p*-nitrobenzenesulphonyl chloride separated in large prisms, m. p. 80° (yield, 70 g.).

The derivatives of this chloride crystallise with remarkable ease. By interaction with alcoholic sodium ethoxide in ethereal solution it gives *ethyl* p-*nitrobenzenesulphonate*, large plates, m. p. 91° (Found :

C, 42·1; H, 3·7. $C_8H_9O_5NS$ requires C, 41·6; H, 3·9%), and with menthol in pyridine *menthyl* p-*nitrobenzenesulphonate*, long needles, m. p. 72° (Found : C, 55·8; H, 6·7. $C_{16}H_{23}O_5NS$ requires C, 56·3; H, 6·7%). The following sulphonates and sulphonamides were obtained by interaction of the components in pyridine solution and crystallisation of the product from acetic acid.

*Phenyl* p-*nitrobenzenesulphonate*, needles, m. p. 114° (Found : C, 51·8; H, 3·4. $C_{12}H_9O_5NS$ requires C, 51·6; H, 3·2%). m-*Nitrophenyl* p-*nitrobenzenesulphonate*, m. p. 133° (Found : C, 44·9; H, 2·5. $C_{12}H_8O_7N_2S$ requires C, 44·5; H, 2·5%). p-*Nitrophenyl* p-*nitrobenzenesulphonate*, m. p. 156° (Found : C, 45·0; H, 2·5%).

*Nitration of Phenyl* p-*Nitrobenzenesulphonate*.—2·5 G. were added slowly to ice-cold fuming nitric acid (5 c.c.), and the resulting solution poured on ice. The precipitate (2·9 g., m. p. 140—150°), when crystallised from acetic acid, furnished *p*-nitrophenyl *p*-nitrobenzenesulphonate (2·4 g.).

p-*Tolyl* p-*nitrobenzenesulphonate*, m. p. 106° (Found : C, 53·7; H, 3·7. $C_{13}H_{11}O_5NS$ requires C, 53·2; H, 3·8%).

3-*Nitro*-p-*tolyl* p-*nitrobenzenesulphonate*, m. p. 136° (Found : C, 46·4; H, 2·9. $C_{13}H_{10}O_7N_2S$ requires C, 46·1; H, 3·0%).

2-*Nitro*-p-*tolyl* p-*nitrobenzenesulphonate*, m. p. 116° (Found : C, 45·9; H, 3·0%).

*Nitration of* p-*Tolyl* p-*Nitrobenzenesulphonate*.—4·5 G. were added to fuming nitric acid (10 c.c.) and the solution was poured on ice. The resulting precipitate (m. p. 100—110°; 3·6 g.) on crystallisation from acetic acid furnished 2-nitro-*p*-tolyl *p*-nitrobenzenesulphonate (2·5 g.).

p-*Nitrobenzenesulphon*-p-*tolylamide* has m. p. 179—180° (Found : C, 54·0; H, 3·7. $C_{13}H_{12}O_4N_2S$ requires C, 53·5; H, 4·1%). This compound (2·5 g.) and nitric acid (5 c.c.) were warmed on a steam-bath until a vigorous reaction took place. The mixture was diluted with water and the precipitate obtained, on crystallisation from acetic acid, gave p-*nitrobenzenesulphon*-3 : 5-*dinitro*-p-*tolylamide* (XIV), m. p. 185° (Found : C, 40·8; H, 3·0. $C_{13}H_{10}O_8N_4S$ requires C, 40·8; H, 2·6%), which was identified by hydrolysis to 3 : 5-dinitro-*p*-toluidine (acetyl derivative, m. p. 194°).

5-*Acetoxymercuri*-2-*acetamidodiphenyl*.—To a solution of 2-aminodiphenyl (5 g.) in alcohol (40 c.c.) was added mercuric acetate in water (40 c.c. containing acetic acid, 2 c.c.). The precipitated oil, after being dried, was warmed with acetic anhydride; the product crystallised from aqueous acetic acid in needles, m. p. 200° (Found : Hg, 43·2. $C_{16}H_{15}O_3NHg$ requires Hg, 42·7%). Treated with bromine in acetic acid, this compound gave 5-bromo-2-acetamidodiphenyl, crystallising from aqueous alcohol in long needles,

m. p. 128°, identical with the compound prepared by the method of Scarborough and Waters (*loc. cit.*).

*Mercuration of* 4-*Aminodiphenyl.*—Mercurated by the method described above, 4-aminodiphenyl gave a white precipitate, m. p. 167° (Found: Hg, 54·7%), which crystallised from aqueous acetic acid without change (Found: Hg, 54·8%). It appears to be the substance $C_6H_5 \cdot C_6H_3 \begin{smallmatrix} NH \\ | \\ Hg \end{smallmatrix}$, which requires Hg, 54·6%. Its solution in warm acetic acid, on cooling, deposited needles of 3-*acetoxymercuri*-4-*acetamidodiphenyl*, m. p. 205° (Found: Hg, 42·9. $C_{16}H_{15}O_3NHg$ requires Hg, 42·7%). On repeated crystallisation from boiling acetic acid this compound lost its crystalline character and increased in melting point and mercury content (44·1, 46·5%). The product, m. p. 205°, on treatment with bromine (1 mol.) in acetic acid gave gummy material, but with an excess of bromine it gave a compound, sparingly soluble in alcohol and crystallising from benzene in colourless needles, m. p. 196°. This must be 3 : 4′-dibromo-4-acetamidodiphenyl (Scarborough and Waters, J., 1926, 561), and the presence of this additional bromine atom accords well with the propensity of 4-acetamidodiphenyl to brominate in the 4′-position.

*Bromination of* 4-p-*Toluenesulphonamidodiphenyl.*—To 6 g. in warm acetic acid (50 c.c.) was added bromine (3 g.) in acetic acid (15 c.c.). After cooling, the solution was filtered from a small amount of unchanged material and poured into water. The gummy precipitate, after repeated crystallisation from alcohol, gave 3-*bromo*-4-p-*toluenesulphonamidodiphenyl* in large prisms, m. p. 119° (Found: C, 56·4; H, 4·2. $C_{19}H_{16}O_2NBrS$ requires C, 56·7; H, 4·0%). It was identical with the compound obtained by the interaction of *p*-toluenesulphonyl chloride and 3-bromo-4-aminodiphenyl in pyridine solution.

3-Bromo-4-hydroxydiphenyl furnished a uniform *monomercuri*-derivative, which crystallised from acetic acid in needles, m. p. 235° (Found: Hg, 39·7, 39·4. $C_{14}H_{11}O_3BrHg$ requires Hg, 39·5%), but 4-hydroxydiphenyl gave a mixture of more highly mercurated derivatives (Found: Hg, 61·7, 60·6. $C_{16}H_{14}O_5Hg_2$ requires Hg, 58·4%). When treated with bromine in acetic acid, these compounds all gave 3 : 5 : 4′-tribromo-4-hydroxydiphenyl.

3-*Acetoxymercuriaceto*-p-*toluidide.*—Mercuric acetate (20 g.) was added to aceto-*p*-toluidide (10 g.) in acetic acid (100 c.c.) and the solution, after boiling under reflux for 1 hour, was filtered from precipitated mercurous acetate and evaporated under diminished pressure. The residue was boiled with water and crystallised successively from aqueous alcohol, acetic anhydride, and acetic acid,

3-*acetoxymercuriaceto*-p-*toluidide* being obtained in long needles, m. p. 178° (Found: Hg, 49·3, 49·6. $C_{11}H_{13}O_3NHg$ requires Hg, 49·3%). It was more easily prepared by dissolving 3-acetoxymercuri-*p*-toluidine (m. p. 189° decomp.: obtained in quantitative yield from *p*-toluidine) in acetic anhydride, and recrystallising the product until of constant melting point. Treated with bromine in acetic acid, it gave 3-bromoaceto-*p*-toluidide contaminated by dibromoacetotoluidide.

Wellcome Chemical Research Laboratories, London, E.C. 1.
Battersea Polytechnic, London, S.W. 11.

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